

Use of Ab Initio Interaction Energies for NRTL to Predict Phase Equilibria in the System Nitrogen - Ethane

G. Raabe ^{C, S} and J. Koehler

Institut fuer Thermodynamik, TU Braunschweig, Braunschweig, Germany

Equations of state or activity coefficient models for the determination of phase equilibria usually contain adjustable parameters. These parameters are determined by regressions of experimental data, limiting the models by the availability and accuracy of these data. Sum and Sandler [1] succeeded in using ab initio molecular orbital calculations of interaction parameters of the UNIQUAC activity coefficient model. They calculated interaction energies on the HF/6-311++G(3d,2p) method level to predict phase equilibria in systems containing polar components. In the present work ab initio interaction parameters are firstly used to predict phase equilibria in a system with a van der Waals dominated interaction. The calculation of the weak interaction energies in the system nitrogen-ethane requires high level ab initio methods which account for electron correlation. The dimer minimum energy structure for different intermolecular orientations are determined using the MP2 method. The interactions of these minimum-energy configurations are calculated on the MP4 and QCISD(T) theory level. The energies are then used as the interaction energy parameters in the NRTL-model. Predictions of the high-pressure VLE and VLLE are made using the Peng-Robinson and the Soave-Redlich-Kwong equation of state and a different G^E -mixing rule.

[1] Sum, A.K. and Sandler, S.I. A Novel Approach to Phase Equilibria Predictions Using Ab Initio Methods Ind. Eng. Chem. Res. 1999, 38, 2849-2855.